

CEMENT AND LIME MANUFACTURE

Vol. XXXII. No. 2

MARCH, 1959

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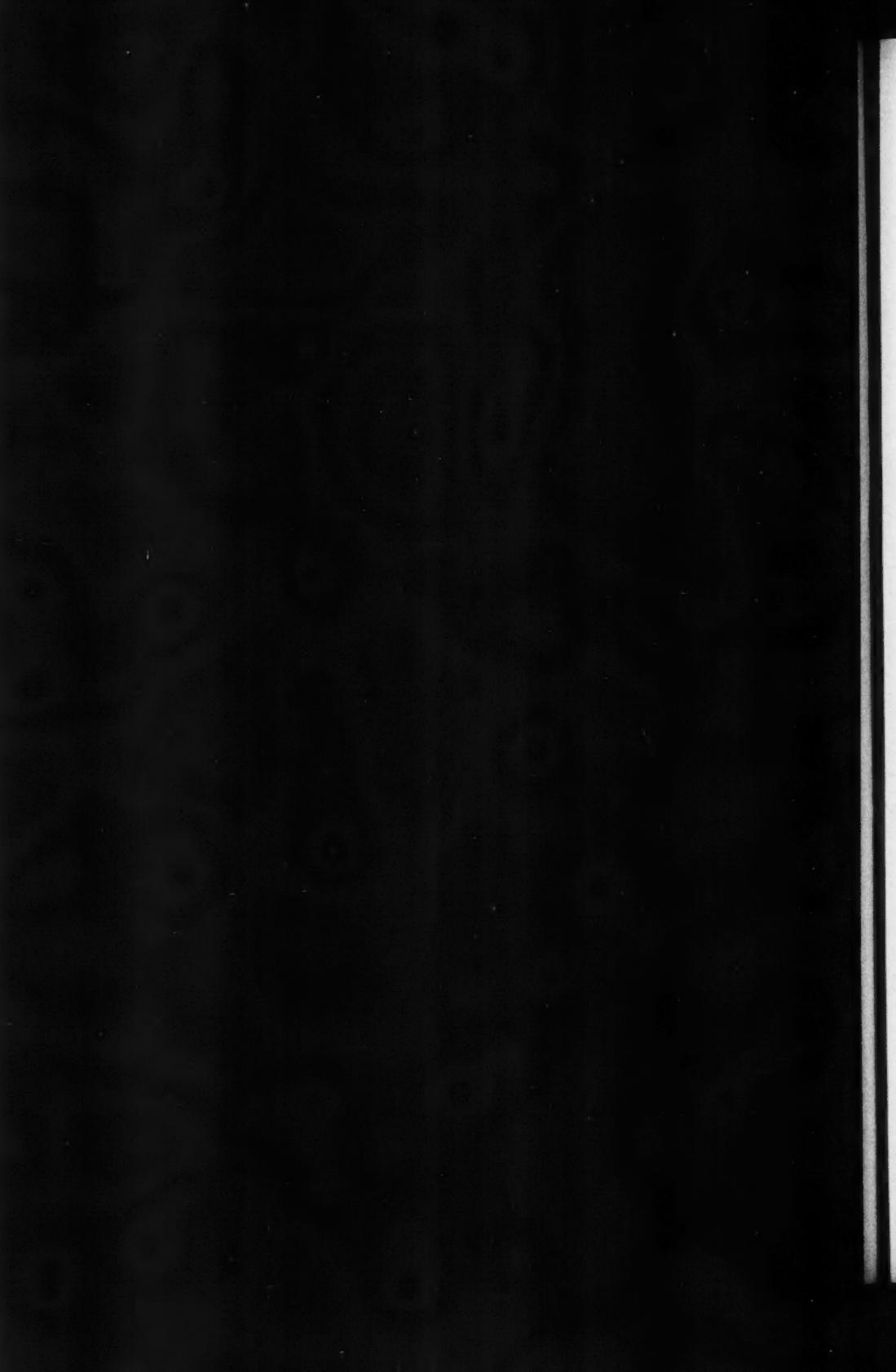
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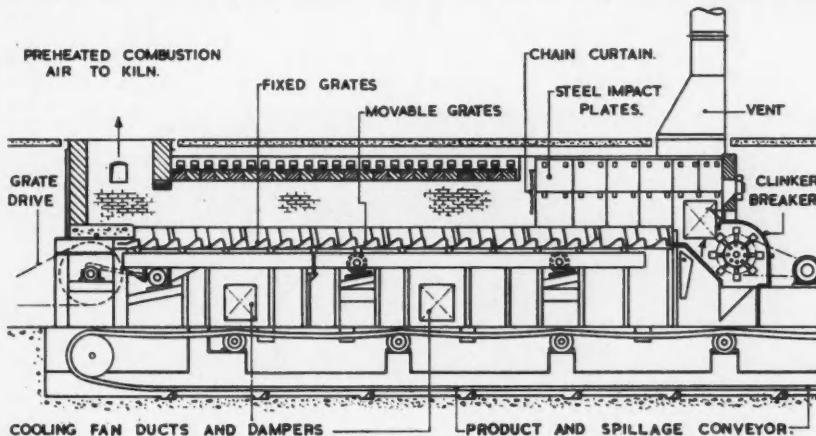
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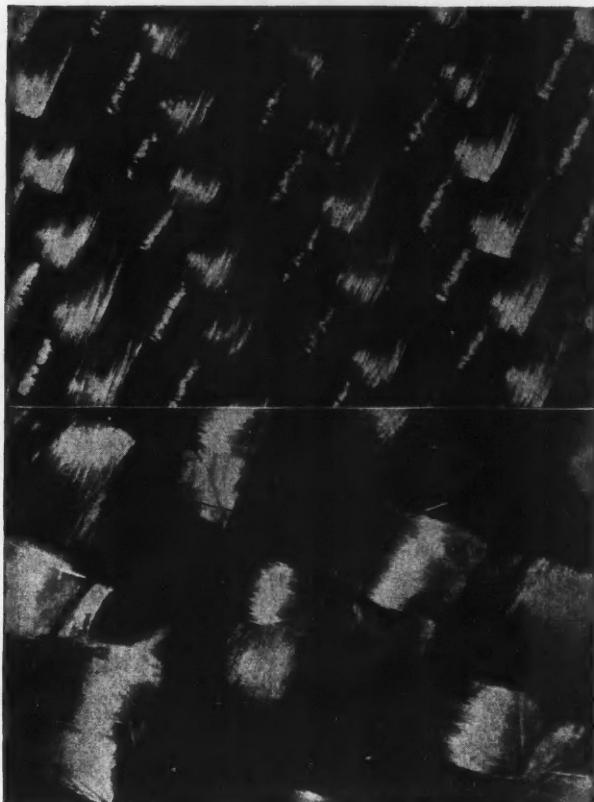
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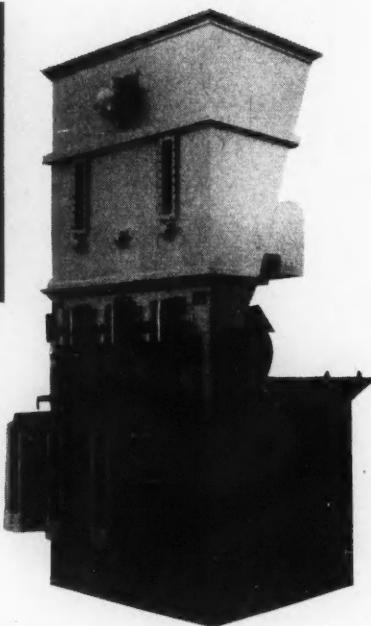
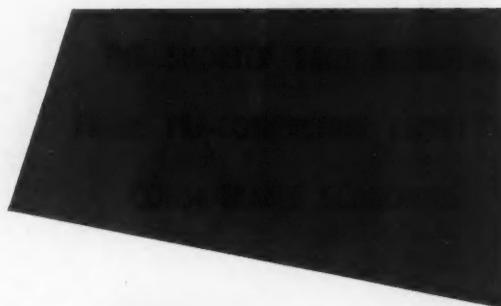
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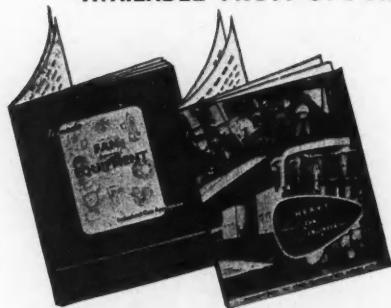
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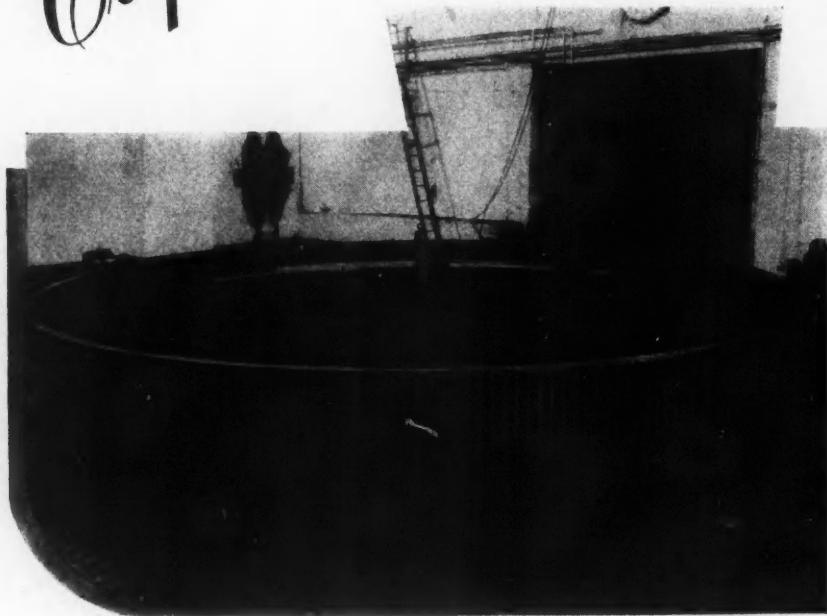
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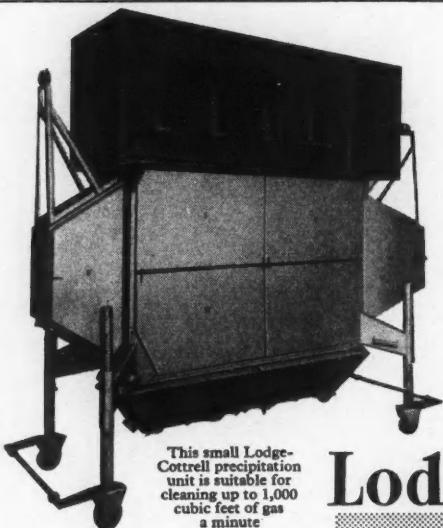
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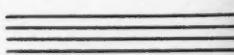
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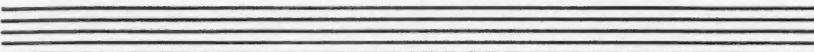
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MARCH, 1959

Trief Concrete Used in a Dam.

THE provision in the Avon dam in Devonshire of 100,000 cu. yd. of Trief concrete comprising 12,000 tons of slag-slurry and cement mixture is described by Mr. J. M. Bogle, Mr. R. M. Ross, and Mr. T. McMillan in the Proceedings of the Institution of Civil Engineers for January, 1959. The object of using this concrete was to reduce the heat of hydration and thereby expedite construction. [The Trief process as used for two dams in Scotland was described in this journal for May, 1954.]

Granulated Slag.

The blastfurnace slag was produced at the Appleby-Frodingham steelworks by sudden quenching of hot molten blastfurnace slag with high-pressure jets of cold water. The slag had the appearance of coarse sand, and a typical chemical composition was (in percentages): Moisture, 3.60; silica, 34.93; insoluble residue, 0.67; alumina (containing 1.44 per cent. manganese oxide), 18.02; ferric oxide, 1.18; lime (CaO), 40.98; magnesia, 3.55; alkalis and loss, 0.67. Total sulphur expressed as SO₃, 2.75 per cent.; sulphur present as sulphide (S), 1.10 per cent.

In the course of some notes on this type of concrete the authors state that in addition to consistent chemical composition the slag must be granulated in such a manner that its vitreous condition is maintained since this property affects the rate of gain of strength of the concrete. The granulation depends on the temperature of the furnace, the size and power of the water-jet, and the skill of the operator. Tests for vitreosity were made at the site by means of a Woods-Light apparatus in which the colour of the sample as shown by ultra-violet light is compared with a series of standard glasses.

Ground-slag Slurry.

At the site of the construction of the dam, the slag was ground in a rotating ball mill (*Fig. 1*), 30 ft. long and 5 ft. in diameter, to an average specific surface

of 3500 sq. cm. per gramme. The mill was rotated by a 225-h.p. electric motor. Each of the three compartments contained 18 tons of steel balls in sizes up to 4 in. diameter. Wear of the balls necessitated periodical regrading and replacement; the rate of wear of the balls was about 7 lb. for each ton of slurry. The maximum output of the mill was 3 tons per hour. The slag and water were delivered to the mill automatically; the water content was about 30 per cent. The temperature of the mill was kept below boiling point by air cooling. The slurry passed along a launder into three storage tanks each 16 ft. square and 8 ft. deep, and each contained enough for one day's concreting. The slurry in the tanks was kept continually agitated by air jets, pumped from the tanks along a 4-in.

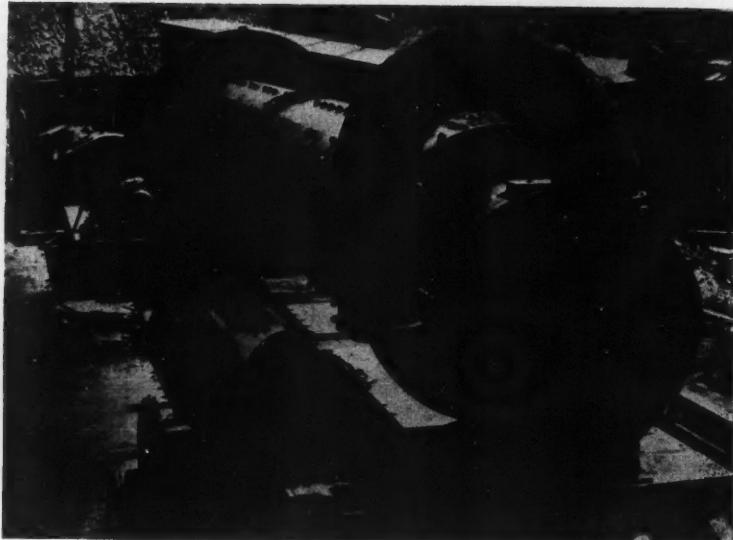
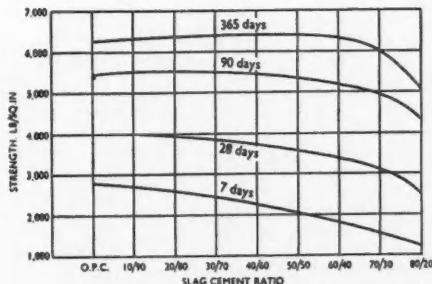
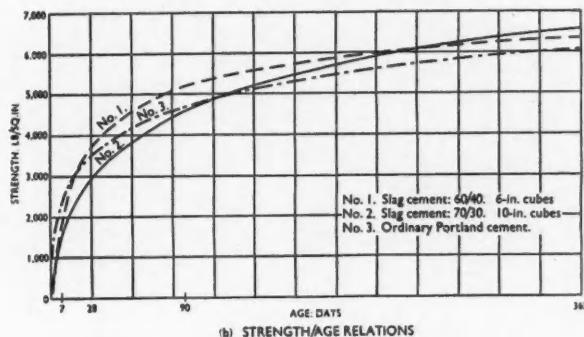


Fig. 1—Ball Mill on Construction Site.

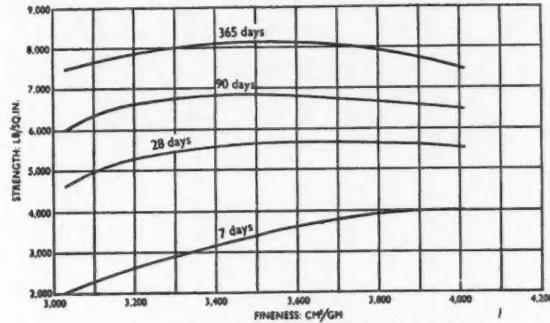
pipe, and discharged into the drum of the concrete mixer at the same time as the Portland cement. The water content of the slurry was maintained within close limits, since if it exceeded 30 per cent. the concrete became too sloppy and if it were less than 27 per cent. the slurry tended to clog in the pipe and settle in the corners of the tanks.

The Concrete Mixture.

The mixture for the hearting concrete in the dam was 70 per cent. slag-slurry and 30 per cent. ordinary Portland cement. A characteristic of Trief concrete is the slow development of strength and, to enable the shuttering to be removed in a reasonable time in cold weather, calcium chloride was added in the proportion of $1\frac{1}{2}$ per cent. by weight of the slurry-cement mixture. With the accelerator

(a) STRENGTHS OF 4-IN. CUBES WITH $\frac{1}{2}$ IN. AGGREGATE

(b) STRENGTH/AGE RELATIONS



(c) B.S. MORTAR TESTS. SLAG CEMENT RATIO: 70/30

Fig. 2.

the compressive strength at seven days increased by 40 per cent., but there was no gain in strength after about sixty days.

Fig. 2a shows the results of site tests of 4-in. cubes with $\frac{1}{4}$ -in. aggregate, and indicates the crushing strengths for various slag-cement ratios at periods up to one year. Generally it was found that the strength was reduced rapidly with proportions of slag more than about 75 per cent. *Fig. 2b* shows the gain in strength with age of site-made 10-in. concrete cubes with ordinary aggregate; the curve for ordinary Portland cement is from the Road Research Laboratory's Road Note No. 4.

The fineness to which the slag is ground influences the early strength to a marked degree, as is shown by *Fig. 2c*. At the start of the work the slag was ground to a fineness of 4500 sq. cm. per gramme, but later this was reduced to about 3500 sq. cm. per gramme. For a short period the fineness was nearly 3000 sq. cm. per gramme and marked reduction of early strength took place; one or two failures occurred during testing.

Heat of Hydration.

The heat of hydration of the ordinary Portland cement used throughout the works and of mixtures of slag-slurry and cement were as in *Table I*.

TABLE I. HEAT OF HYDRATION. (Calories per gramme.)

Ordinary Portland cement	100 per cent.	40 per cent.	30 per cent.
Slag-slurry	Nil	60 per cent.	70 per cent.
At 7 days	73	48	46
At 28 days	77	55	51

Twenty-four thermometers of the platinum-resistance type were built into the concrete in various positions and records were kept for more than nine months. The rise in temperature in the Trief concrete was about 65 per cent. of that of Portland cement concrete. An average rise was about 25 deg. F. in the case of Trief concrete in the centre of a 4-ft. lift of concrete if other lifts were superimposed after a short interval. The use of ordinary Portland cement alone would have delayed the placing of concrete in adjacent bays to intervals of eight weeks and successive placings to intervals of six days. By using Trief concrete these times were reduced to eight days and three days respectively.

The Japan Cement Engineering Association.

The report of the general meeting of the Japan Cement Engineering Association, held in Tokyo in May 1957, is now available from the Association at No. 1 Akasaka-Daimachi Minatoku, Tokyo. An address on "The Use of Cement in Concrete", by Dr. R. H. Bogue of the U.S.A., is printed in full, and synopses are given of seventy-eight papers on the chemistry and manufacture of cement; most of the papers describe recent research undertaken in Japan at universities and in the laboratories of cement makers.

The System Lime-Alumina-Water.

A STUDY of phase equilibria in the system $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ at 1 deg. C. has been made by Mr. Elmer T. Carlson, and the results are reported in Research Paper No. 2877 of the U.S. National Bureau of Standards.

The author points out that there has been a great deal of research into the system lime-alumina-water, largely because of its relation to the setting and hardening of hydraulic cements, but among the questions left unsettled are the following: (1) The existence of an hexagonal tricalcium aluminate hydrate, usually formulated $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 12\text{H}_2\text{O}$, is considered to be well-established by many authorities, but others have concluded that the supposed compound is actually a mixture of the dicalcium and tetracalcium aluminate hydrates. (2) The existence of more than one form of tetracalcium aluminate hydrate. (3) The area of stability, or metastability, of monocalcium aluminate hydrate. Although the formation of such a compound was reported many years ago, its existence has been confirmed only recently, and none of the published phase diagrams shows any stability area for it.

The present study was undertaken in the hope of shedding further light on these and other questions. The temperature of 1 deg. C. was selected because one investigator had indicated that the formation of monocalcium aluminate hydrate was favoured by low temperature. Insofar as the information gained may be related to the practical problems of hydraulic cements, temperatures near the freezing point are occasionally encountered during the placing and hardening of concrete.

The study showed that the stable phases appear to be gibbsite ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}_3$), $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 13\text{H}_2\text{O}$, and $\text{Ca}(\text{OH})_2$. Metastable equilibrium curves were determined for $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 8\text{H}_2\text{O}$ and $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$. A metastable invariant point for the last two hydrates and solution exists at about 0.10 gr. of Al_2O_3 and 0.38 gr. of CaO per litre. The compounds of $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 8\text{H}_2\text{O}$ and $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 13\text{H}_2\text{O}$ crystallise together over a wide range of concentration, but the former is presumed to be metastable throughout the range. The isometric $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ appears to be metastable at 1 deg. C., being transformed very slowly to one or more of the hexagonal hydrates.

No evidence was found of the existence of an hexagonal tricalcium aluminate hydrate. Only one form of the tetracalcium aluminate hydrate was observed. A similar phase, which was observed in minor amounts in most of the solid residues in contact with solutions, especially after prolonged storage, was identified as a carboaluminate, probably $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaCO}_3 \cdot 11\text{H}_2\text{O}$. The hydrate $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 8\text{H}_2\text{O}$, on being dried over CaCl_2 , was found to lose 2 molecules of water reversibly. The lower hydrate has a characteristic X-ray pattern. Co-precipitated mixtures of $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 8\text{H}_2\text{O}$ and $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 13\text{H}_2\text{O}$, after drying over CaCl_2 , showed lines only of $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 13\text{H}_2\text{O}$ on the X-ray patterns. The dicalcium compound was presumably decomposed to the tetracalcium and amorphous alumina. This reaction was not reversible. Owing to the extreme slowness of dissolution at 1 deg. C. the solubility curve of gibbsite was not established.

The author states that the system $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ is not directly applicable to Portland cement, which is predominantly a calcium silicate cement with enough calcium sulphate added to combine with most of the alumina in the early stages. On the other hand, it has been shown that the hydration of high-alumina cements, at least to a first approximation, can be explained in terms of reactions in the system $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$. High-alumina cements are known to react with water to form highly supersaturated calcium aluminate solutions slightly more basic than monocalcium aluminate. The crystalline phase that precipitates first may be $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$ or $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 8\text{H}_2\text{O}$, or a mixture of these, depending on temperature, basicity, and probably other factors. It may be concluded that, at 1 deg. C., $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$ would either precipitate first or form rapidly after an initial precipitation of the dicalcium compound. Earlier work indicates that, at room temperature, $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 8\text{H}_2\text{O}$ forms initially and persists for long periods. However, it is clear from other data that the reactions of cement in paste form are not necessarily identical with those in the presence of a large excess of water. Thus $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$, rather than $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 8\text{H}_2\text{O}$, was shown by X-ray diffraction to be the predominant phase in pastes of high-alumina cements after hydration at room temperature (24 deg. C.). From the data in the present report and that in an earlier paper it is concluded that monocalcium aluminate hydrate is also the chief crystalline product of hydration of high-alumina cements at 1 deg. C.

In connection with the hydration of cements the carboaluminate $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaCO}_3 \cdot 11\text{H}_2\text{O}$ should also be mentioned. It is apparent that this phase was encountered throughout the range of lime concentrations studied, despite efforts to exclude CO_2 . Most other investigators likewise have sought to eliminate the extra component. In practice, however, cement is always mixed and placed in the presence of atmospheric CO_2 , hence the carboaluminate may form freely. Evidence of this has been found in the X-ray patterns of hardened pastes of high-alumina cements. In a previous study it was reported as "phase x"; the position of the diffraction lines now permits its identification as the carboaluminate.

Some recent investigations into the nature of the contact film between hardened cement and aggregate are also of interest in this connection. It has been found that high-alumina cement appeared to react superficially with calcite aggregate. The X-ray pattern of the reaction product included a series of lines that agree well with the pattern obtained in the present study for the carboaluminate. One investigator was of the opinion that the pattern indicated the presence of a solid solution between $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 13\text{H}_2\text{O}$ and a carboaluminate. Such a composition had been previously suggested by another investigator for the mineral hydrocalumite. In the present work, however, and solely on the basis of the X-ray patterns, the carboaluminate and $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 13\text{H}_2\text{O}$ appear to exist side by side, with no evidence of solid solution between the two.

These questions cannot be resolved without further data. There can be little doubt, however, that carbon dioxide may play a significant role during, and subsequent to, the hardening of high-alumina cements, and probably of other hydraulic cements.

Woven-glass Filter Bags.

WOVEN-GLASS fabrics treated with silicones have been used in some industries for collecting dust at high temperatures, and have more recently been installed in some of the works in the U.S.A. of the South-western Portland Cement Company. It has been found that this material is satisfactory at temperatures up to 500 deg. F., so that it is not necessary to cool the gases before they come into contact with it as is the case with the material generally used for filter-bags in cement works.

An experiment was made of installing woven-glass filter-bags in an exhaust flue where the temperature was 500 deg. F. During a period of nine months the result was satisfactory, and it was found that, due to the smooth surface of the bags, no shaking was necessary to remove the dust. The bags were at times saturated with water due to condensation, but suffered no ill-effects and dried with rise of temperature. The experiment suggested that such bags should be serviceable for a year without replacement.

As a result this type of bag-filter was installed at the Company's works at Victorville. The kiln is 300 ft. long by 10 ft. diameter, and operates on the wet process. The exit gases have a temperature of 800 deg. F. to 900 deg. F., and flow vertically to a dust-collector of the multiple-cyclone type, the dust from which is added to the slurry-feeder. From the cyclones about 95,000 cu. ft. of gas per minute at a temperature of 550 deg. F. flow downward to an induced-draught fan which discharges through a horizontal duct of 6 ft. 3 in. diameter in which a Y-shaped diversion was fitted to the inlet of the bag-house. The bag-house is of the pressure type and contains six hoppers arranged in two parallel rows of three each, and an inlet balloon-flue extends between the two rows. In each hopper there is a partition to form two compartments, each of which is connected to the flue by a duct of 2 ft. diameter fitted with a damper. The dust is removed by a screw-conveyor under each row of hoppers and another under the flue.

In each compartment of the hoppers there are forty-eight steel thimbles of 11½ in. diameter over which the woven-glass filter bags are clamped. At their upper ends the bags are clamped to aluminium caps which are suspended rigidly from steel channels. Wide walkways around each group of 48 bags are provided at the thimble level and also a few feet below the caps for ready access and ease of installation. There are 576 bags in all and, with an effective length of 25 ft., the total filtering area is about 43,000 sq. ft. The bag-house is enclosed with corrugated asbestos-cement sheets to maintain the gas temperature as high as possible, and the filtered gas leaves through an open space between the sides and the roof. Diffusion into the atmosphere is so rapid that no condensation occurs, and the discharge is normally invisible.

No shaking mechanism is provided, the bags being discharged by a simple periodical collapse produced by an independent suction system. Each compartment is connected through horizontally-acting dampers to 20-in. ducts leading to the suction side of an auxiliary fan, which discharges in turn into the balloon-

flue. Thus each compartment has two dampers, one an inlet damper and the other a suction damper. Each group of bags collapses once every hour. The cycle requires about one minute and is as follows: (1) the inlet damper closes; (2) the suction damper opens, creating a negative pressure in the compartment and causing the bag to collapse; (3) the suction damper closes, the bags are slowly re-inflated, and dust falls into the hopper; (4) the inlet damper opens. While both dampers are closed gas from the adjacent compartment leaks in around the screw-conveyor connection and slowly inflates the bags; this permits the free discharge of dust caught in the folds of the collapsed bag.

The average conditions in the bag-house are as follows. Each minute 90,000 cu. ft. of gas at 510 deg. F. enter the balloon-flue. The overall reduction of pressure across the bags is about 3 in. water-gauge, which has shown little or no change in twelve months of operation. No discharge is visibly detectable, and the bags have remained almost perfectly clean and white on the outside. It is possible to walk about freely at the thimble level without discomfort or danger. At the upper level the gases are mixed and, as a safety precaution, entry is permitted only with a breathing apparatus. The collected dust was first wasted, but a mixer has been devised to permit the dust to be added continuously to the slurry and returned to the kiln. Normal variations of pressure have no appreciable effect on the operation of the kiln. After nine months of operation sixteen of the 576 bags had been replaced; no failure was due to deterioration by heat or abrasion. Similar bag-houses are to be installed at three more kilns at this works.

At the Company's works at El Paso two dry-process rotary kilns were equipped with bag-houses. The gases from centrifugal collectors were led down to induced-draught fan inlets at ground level, then upward to the bag-houses (one for each kiln) on top of the structure. The bag-houses were pressure-type units and were fully exposed. Each was fitted with 792 6-in. by 16-ft. orlon bags with vertical shakers. Because of the difficulty of cooling the gases to 275 deg. F. woven-glass filter bags were installed. The shaking mechanisms previously used were removed and the bags discharged by collapsing them. Suction for collapsing the bags is provided by an auxiliary fan through an entirely separate system, and the bags are cleaned on a 5-minutes' cycle. The inlet temperatures of the gases are normally from 600 deg. to 700 deg. F., with an automatic by-pass for protection against extremes which may develop from interruptions in kiln feed. Moderate variations are controlled by the automatic operation of a tempering air damper at the inlet to the induced-draught fan.

The Cement Industry in Bolivia.

It is reported that a cement works at Sucre, which is owned jointly by the Government Development Corporation, the University, and the municipality of Sucre, is ready for operation as soon as capital can be found for the purchase of sacks.

The Cement Industry in Europe.

THE Organisation for European Economic Co-operation (O.E.E.C.) has issued a report entitled "The Cement Industry in Europe 1957" which is obtainable (price 6s.) from the office of the Organisation at 2 Rue André-Pascal, Paris 16. The Organisation comprises the following member countries: Austria, Belgium, Denmark, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, the Netherlands, Norway, Portugal, Sweden, Switzerland, Turkey, and the United Kingdom.

In the year 1957 the total production of cement in these countries was 75,600,000 tons, which is an increase of 1,100,000 tons compared with the year 1956. The increase was less than in the preceding two years; production in the year 1956 was 4 per cent. more than in 1955, and in 1955 production was 12 per cent. more than in 1954. Compared with the year 1956, production fell by 6 per cent. in the United Kingdom and by 2 per cent. in Germany. There were increases of 11 per cent. in France and 6 per cent. in Italy.

During the year 1957 thirteen new cement works were built in the member countries. Of these two were in Germany, each equipped with a rotary kiln and having a total annual capacity of 250,000 tons; five were in Italy, one of which is a conversion of an old lime works and has a total annual capacity of 275,000 tons (two of the new works have rotary kilns and the rest have vertical kilns); one was in the United Kingdom equipped with a rotary kiln with a capacity of 231,000 tons a year, and five were in Turkey, all having rotary kilns with a total capacity of 485,000 tons a year.

The number of manual workers employed in the industry in 1957 was reduced by about 600 compared with 1956 in spite of the increased production, but the number of clerical and administrative workers increased by more than 800. The average production per man employed increased from 794 tons in 1956 to 800 tons in 1957.

The total consumption of cement in the member countries was about equal to production; at 72,052,000 tons, consumption was about 2 per cent. more than in 1956. In France consumption increased from 10,900,000 tons to 12,400,000 tons; other increases were 24 per cent. in Turkey, 12.5 per cent. in Austria, 6 per cent. in the Netherlands, 7.3 per cent. in Portugal, 5.6 per cent. in Norway, 5.2 per cent. in Italy, and 2.8 per cent. in Switzerland. Consumption decreased by 5.7 per cent. in the United Kingdom and by 2.3 per cent. in Germany.

In 1957 exports from the member countries were 9 per cent. less than in 1956, and represented 7.7 per cent. of production compared with 8.5 per cent. in 1956 and 10.5 per cent. in 1955. This was due to the production of cement in countries that formerly depended upon imports, and competition from Japan and countries in East Europe.

The price of cement was reduced in 1957 (compared with 1956) by 10 per cent. in Greece and there was a slight reduction in Denmark. In Italy there was no change, and there were increases in the other member countries.

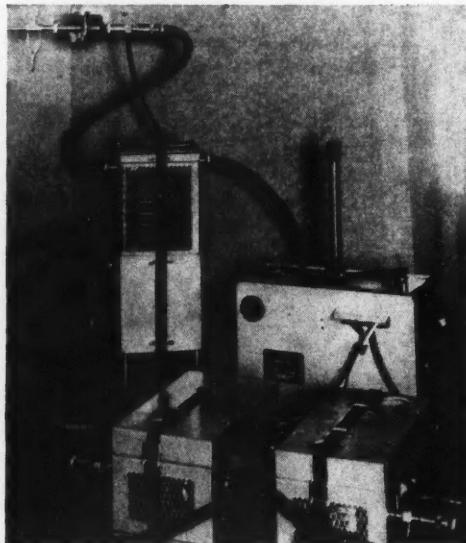
In the first nine months of the year 1958 there was a reduction of exports of 20 per cent. compared with the same period in 1957.

Generally speaking, estimates made in 1956 for the construction of new works in 1958 have been adhered to, except in the case of Italy where one works equipped with a rotary kiln was built instead of two new works, thus increasing total capacity by 150,000 tons, instead of 230,000 tons. In Turkey, two of the seven works proposed have not been proceeded with, so that production will be increased by 425,000 tons instead of 660,000 tons. In Denmark, France, Iceland, and Switzerland the programmes were unchanged; in each of these countries it was proposed to construct one new works in 1958 with capacities of 135,000 tons, 180,000 tons, 78,000 tons and 110,000 tons respectively.

In 1959 it is planned to start five new works in Italy with a total capacity of 1,450,000 tons, each equipped with a rotary kiln, and in Turkey it is proposed to build three new works. This year it is also proposed to install a new wet-process rotary kiln at an existing works in Belgium.

The Sampling of Dust.

THE apparatus described in this journal for July 1958 for measuring the concentration of dust and fume is now being made by the Longworth Scientific Instrument Co., Ltd. The complete sampling train is shown below; in the background



are the cooling core (on the left) and the instrument unit, and in the foreground are the two pumps. The filter is in the top corner.

It is stated that the apparatus can be operated by one man and that the filter can be changed in ten seconds. Two-column tables are used to relate the gauge reading to the isokinetic sampling rate, so that few calculations are necessary.

The Contraction during Hardening of Systems of Cement and Water.

EXPERIMENTS in which the progress of the total contraction of a system of Portland cement mortar in water was correlated with the growth in strength of the mortar are described by W. Czernin in a recent number of "Zement-Kalk Gips".

Measurements of the contraction were made in volumeters which comprised glass flasks with flat bottoms, vertical sides, and wide necks ground to receive stoppers. Each stopper carried a microburette of 10 c.c. capacity. The mortars were placed in short wide reaction tubes, three of which could be placed mouth upward in each flask. Entrained air was removed by allowing the charge to flow down the side of the reaction tube while it was vibrated. The total amount of mortar was determined by weighing. After the tubes had been inserted, the volumeter was filled with water without disturbing the surface of the paste in the tubes. A series of volumeters was placed in a bath and maintained at 20 deg. C. plus or minus 0.1 deg. C.

The total volume of a cement-water system decreased rapidly in the early stages, but when the cement had hardened a constant volume of about 6 c.c. for every 100 gr. of cement was approached. Ordinary concrete and specimens of mortar sealed with paraffin wax had much smaller contractions. The contraction of the cement-water system corresponded to the difference in volume between the reactants and the products of reaction. For every 4 gr. of free water chemically bound (that is water which becomes "unevaporable"), the reduction in volume was 1 c.c. Since the strength was broadly proportional to the fraction of gauging water which became combined chemically, it was reasonable to suppose that contraction of the system of cement-water could be related to strength.

In tests to determine the effect of initial water-cement ratio, the contraction was determined with neat cement pastes with water-cement ratios of 0.4 and 0.8. After seven hours the contractions were c. 4 and 0.6 c.c. respectively, and after twenty-eight days 4.40 and 5.56 c.c. Subsequent experiments were carried out with a water-cement ratio of 0.6, when sedimentation of the paste occurred during vibration; to avoid this quartz ground to the fineness of the cement was added to obtain a definite consistency. Different cements required different amounts, but with mixtures in the range 1:1:1 and 1:1:4 the overall variation in the contraction at twenty-eight days was within 2 per cent. At earlier ages the variation was somewhat larger.

Determination of the contractions of several cements showed that the more active cements had greater contraction, but that there was an overall non-linear relation between strength and contraction. With increasing strengths the contraction approached a limit of 6 c.c. per 100 gr. of cement. This effect might have been connected with the earlier hardening of the cement nearer the surface of the specimens.

When similar tests were made with the same cements at 2 deg. C. the contractions at corresponding strengths were greater, with a less steep approach to

the final value of somewhat over 7 c.c. per 100 gr. of cement. This result suggests that the hydrates formed at lower temperatures contain more water and have lower strengths.

The Cement Industry in Japan.

A BROCHURE issued by the Japanese Cement Association gives some interesting notes on the development of the cement industry in Japan with many photographs of old and new cement works and important concrete structures. The first cement works, with shaft kilns, was built in Japan in the year 1880. To-day Japan is the fourth largest cement-producing country in the world, following the U.S.A., the U.S.S.R., and West Germany, and followed by France, the United Kingdom, and Italy. One of the reasons for the large production is the prolific deposits of limestone and bituminous coal of suitable quality.

The first rotary kiln was installed early in this century. Production rose from 453,962 metric tons in the year 1910 to 6,199,724 metric tons in 1940. At the end of the war (1946) production was only 927,140 metric tons, but by 1957 it had increased to 15,106,998 metric tons. There are now twenty companies in Japan operating 43 works, some of which are making blast-furnace cement in association with steel works. The average production per factory was 378,000 metric tons in the year 1957; four works produced more than 600,000 tons a year, five produced from 500,000 to 600,000 tons, six produced from 400,000 to 500,000 tons, nine produced from 300,000 to 400,000 tons, and seventeen produced less than 300,000 tons a year. A total of 16,000 people were employed in the industry in 1957. The man-hours required for the production of a ton of cement are 1.75.

Of the total production of cement in the year 1957, 13,579,000 tons were ordinary Portland, 267,000 tons were rapid-hardening, 446,000 tons were moderate heat of hydration, 602,000 tons were blastfurnace Portland, and 213,000 tons were pozzolanic.

The number of kilns installed is 140, of which 73 operate on the dry process, 47 operate on the wet process, 18 are Lepol kilns, and 2 are shaft kilns. Nearly half the total production is made in dry-process kilns. In the coal-fired kilns the coal consumption for calcining, in kilogrammes per metric ton of clinker, in the year 1957 was 254 in the dry-process kilns, 283 in the wet process with short kilns and 230 with long kilns, 147 in Lepol kilns, and 185 in shaft kilns. Because of the high cost of coal there is a tendency to install longer rotary kilns and Lepol kilns, and 140 of the rotary kilns are fitted with air quenching coolers. In the year 1957 the heat consumption per metric ton of clinker in kilo-calories per kilogramme was 1616 in the case of dry-process kilns, 1442 in long wet-process kilns, 1819 in wet-process kilns utilizing waste heat, 1095 in Lepol kilns, and 1107 in shaft kilns, or an average of 1547.

The quantity of cement exported from Japan was 398,000 metric tons in the year 1938. In 1949 exports amounted to 486,000 metric tons, and in 1957 to 2,201,000 metric tons.



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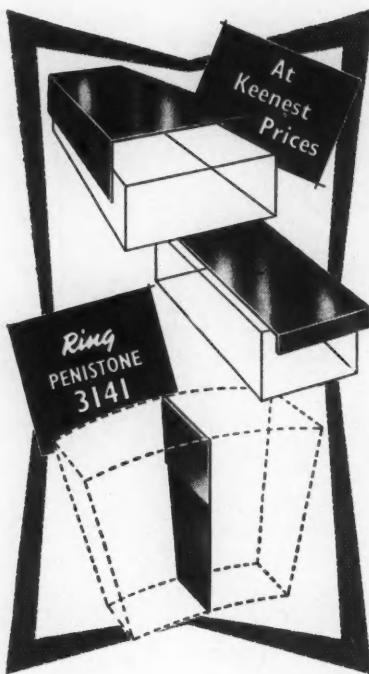
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Patent Applications Relating to Cement.

Burning Cement.

Cement is formed into nodules or agglomerates and introduced into a stream of hot gas to flow concurrently with and in suspension with the gas and to be preheated before being burnt. The hot gas may be that from the rotary kiln in which the burning occurs. The average size of the nodules or agglomerates is not greater than 2 mm.—No. 789,962. F. L. Smidh & Co., Aktieselskab, November 30, 1954.

White Cement.

White Portland cement clinker is obtained by quenching the clinker, after it has left the combustion zone, by immersion in or wetting with an aqueous solution or suspension containing one or more of the acids sulphuric, sulphurous, hydrogen halide, their alkali metal or alkaline earth metal salts or the similar metal salt of sulphylic acid, the quenching period being sufficient to ensure that the white appearance penetrates into the interior of the clinker. Preferred concentration of the liquid is 0.5 to 5 per cent. Reagents adhering to the clinker can be removed by washing with pure water.—No. 788,869. Dyckerhoff Portland-Zementwerke Akt.-Ges., June 15, 1955.

Slag-Cement Concrete.

Concrete containing ground blastfurnace slag of composition 40 to 50 per cent. lime, 14 to 16 per cent. alumina, and 29 to 33 per cent. silica is made by first slurring the finely-ground slag in water, dewatering it to a readily transportable paste having a moisture content of 17 per cent. or less and from which air is excluded, and finally remixing the paste with water, aggregate, and Portland cement or lime.—No. 789,737. F. G. Mitchell, September 6, 1955.

Slag Cement.

Granulated slag is wet ground in the presence of a surface tension reducing agent, for example polyethylene oxide-alcohol condensation products. Admixing with cement or lime gives a cement, and, if aggregate is also added, a concrete.—No. 790,628. F. G. Mitchell and T. E. Rule, September 14, 1955.

Composition of Cement.

Cement is made by burning 100 tons of 5 per cent. calcium carbonate and 5.96 tons of magnesium carbonate with 13.4 tons of coal of 30 per cent. ash content, adding 1.95 tons of gypsum to the resulting clinker, and grinding.—No. 762,606. W. J. Price, May 4, 1954.

Cellular Cement.

Cellular cement is obtained by adding, to an aqueous cement composition, an anionic surface active agent and an ethylene oxide condensation product of either an alkylated phenol or a fatty alcohol. The total addition is from 0.03

to 0.60 per cent. relative to the cement, made up of 15 to 150 parts of the surface-active agent to 100 parts of the condensation product. Specified agents are the alkali metal salts of a long-chain fatty acid, an alkyl-aryl sulphonic acid, a sulphated fatty alcohol, resin acids or tall oil neutralised either with alkali metal hydroxides or amines. Accelerators (for example, calcium chloride), and stabilisers (for example degraded protein and cellulose ethers) may also be present.—No. 787,187. Imperial Chemical Industries, Ltd., October 31, 1955.

Agglomerating Raw Materials.

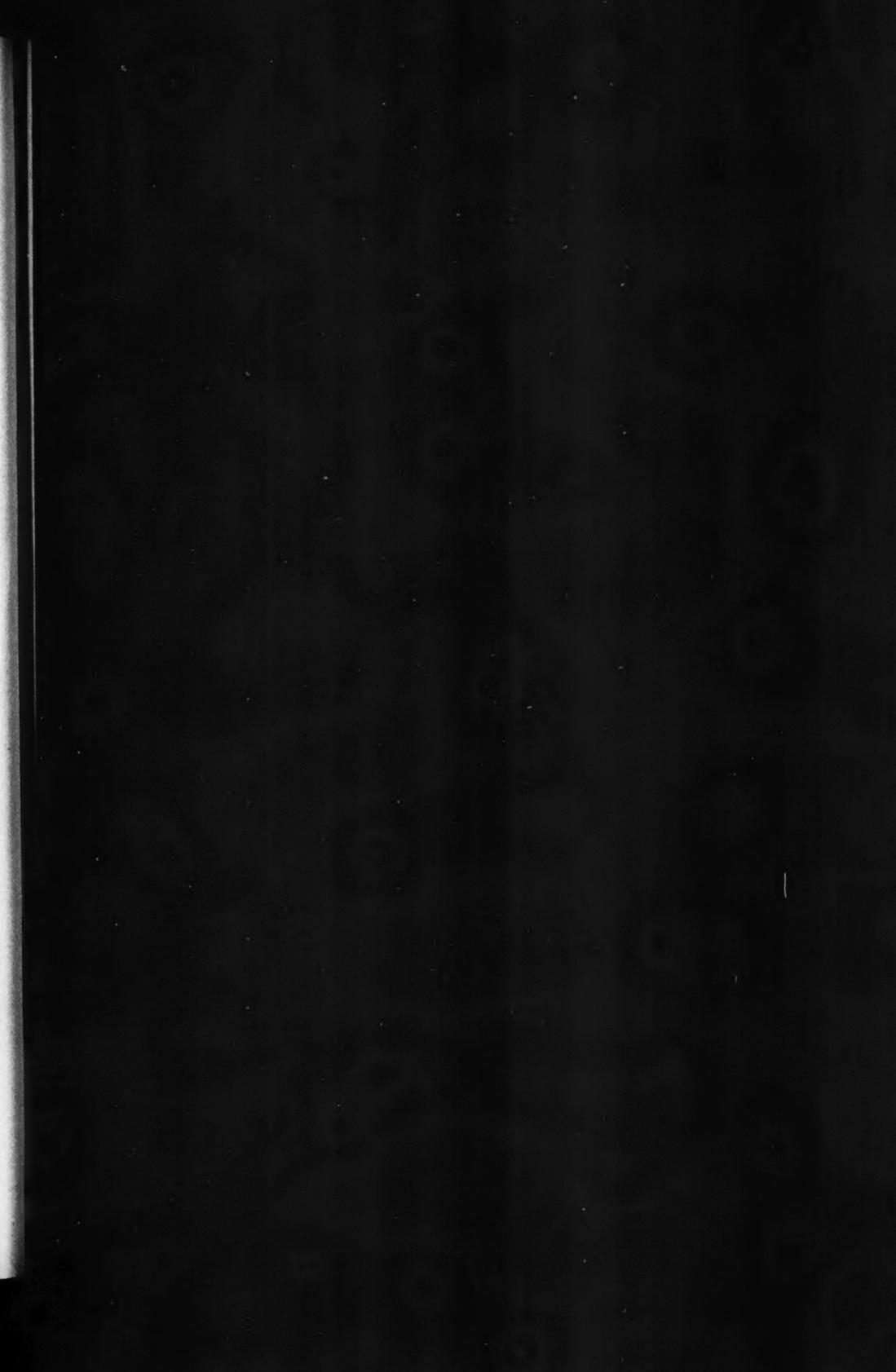
Predominantly finely-ground or pulverulent materials, for example materials for the manufacture of cement, particularly those containing limestone, are agglomerated by adding to the starting material a carbonate of a Group II element if it is not already present, treating the starting material, prior to or following the addition of the carbonates, with hydrochloric acid (for example in the form of a mist) to react with the limestone and added carbonate to form a binder, and shaping the treated material. Carbonate used is preferably limestone of grain size less than 1 mm. In an example, a raw material mixture of calcium carbonate, aluminium silicate, iron oxide, and magnesium carbonate was exposed to hydrochloric acid mist, moulded in a press at 400 kg. per square centimetre, further treated with the hydrochloric acid mist, and dried at 300 deg. C. for one minute.—No. 798,294. H. Burggraf. February 25, 1955.

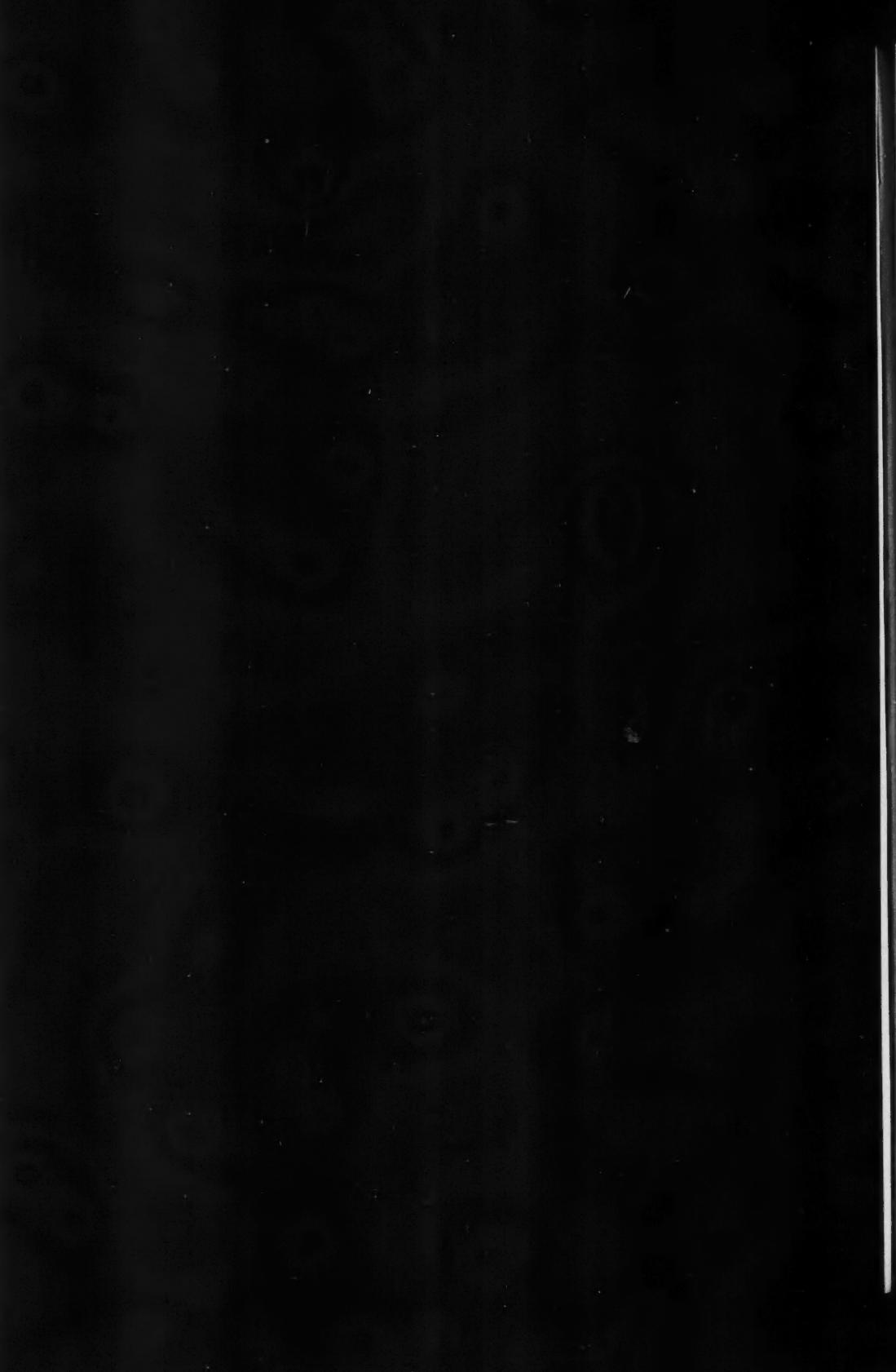
Reducing Sulphates in Cement.

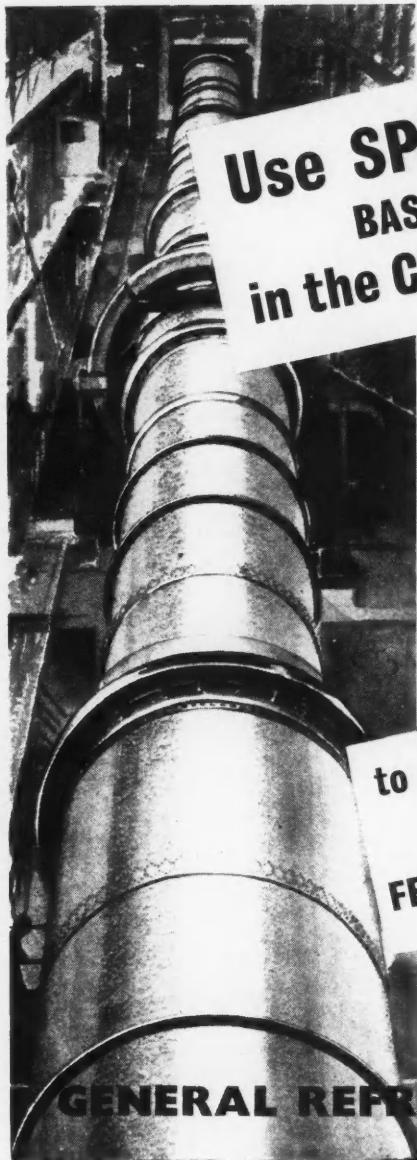
Sulphates present in materials containing also calcium carbonate which are burnt for making cement are reduced by an agent introduced into the materials after they have been at least partly calcined but while they are still being burnt. Reducing agents, for example coke, coal, oil, or gas, may be blown through the discharge end of the kiln, and must be large enough to contact the materials and not be burnt in the flame, but they should not be so coarse that they do not react completely with all the sulphate present, for example not greater than 2 mm. in size. They may be admitted with the fuel.—No. 764,537. F. L. Smidh & Co. Aktieselskab. March 29, 1954.

Burning Cement and Lime.

In a process for burning cement, lime, etc., in shaft kilns, the formation of a compact sintered clinker is avoided by mixing the material with fuel having a grain size less than 1 mm. and forming the mixture into granules or briquettes. A shell of fuel-free raw material is applied around the granules and the treated material is discharged by a rotary grate which tends to break up the clinker and allows uniform air distribution.—No. 781,984. Portland-Zementwerke Heidelberg Akt.-Ges., September 27, 1954.







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